

REFRACTORIES IN THE HANDS OF THE CONSUMER

USE OF TAMPED ZIRCONIUM MASSES FOR LINING VACUUM INDUCTION FURNACES FOR MELTING PRECISION ALLOYS

A. G. Karaulov, N. V. Gul'ko,
B. Z. Pogosov, Yu. A. Gritsianov,*
A. I. Ivanov, and B. A. Matyukhin

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Most high-grade precision alloys are manufactured in vacuum induction furnaces with crucibles based on electromelted magnesite and corundum. Although vacuum furnaces have a number of advantages in comparison with open induction furnaces, they also have shortcomings, including intense reaction of the melted metal with the refractory lining, leading to impairment of the alloy properties.

Recent years have seen extensive research on the development of refractory materials based on electromelted zirconium dioxide, which has a better range of properties for the conditions of vacuum induction melting than traditional refractories. Virtually no work has been done on the use of these refractory materials for crucibles in the melting of precision alloys.

Zirconium dioxide has a high resistance to metals, and during melting of heat-resistant steels and alloys in vacuum it undergoes less reaction with the metal and contamination by oxygen than refractories of Al_2O_3 , MgO , and BeO [1-6]. The oxygen of the oxide can also react with the carbon of the steel and

*Deceased.

TABLE 1. Characteristics of Crucibles after Service

Tamped mass	Durability, melts	Zone*	Crucible composition	Cause of crucible failure
Electromelted zirconium dioxide of PTSB-93 grade based on H_3PO_4	6	Working(5-15)	7-8% magnetite, 5-6% glass, 75% monoclinic ZrO_2 , 10-12% cubic ZrO_2	Appearance of cracks
Electromelted zirconium dioxide of PTSB-93 grade based on s.a.w.	50	Working (10-15)	Cubic ZrO_2 with irregular grains, M magnetite, glass	Incrustation
Electromelted $CaZrO_3$ based on calcium aluminozirconate cement(20%)	3	Working (7-8) †	Metal beads, 4% magnetite, 6% glass, 25% cubic ZrO_2 , 66% $CaZrO_3$	Cracking
		Transition	2% magnetite, 3% glass, 75% $CaZrO_3$, 20% cubic ZrO_2	
		Least altered	92% $CaZrO_3$, 3-4% cubic ZrO_2 , 2% $CaAl_2O_4$, 2% glass	
Electromelted $CaZrO_3$ based on barium aluminozirconate cement	5	Working (4-6) ‡	$CaZrO_3$	Appearance of cracks
		Least altered	$CaZrO_3$, $BaZrO_3$ in binder	

* The zone thickness (mm) is given in parenthesis.

† Cubic ZrO_2 is present nearer to the contact with the metal.

‡ Corroded and glazed, reducing the depth of penetration of iron oxides.

Ukrainian Scientific-Research Institute of Refractories. I. P. Bardin Central Scientific-Research Institute of Ferrous Metallurgy (TsNIChM). Translated from *Ogneupory*, No. 11, pp. 30-33, November, 1980.

TABLE 2. Influence of Crucible Material on Contamination of 008ZhR Metal

Crucible material	Binder	Mass fraction of impurities in metal, * %		
		S	P	Al
Zirconium dioxide	5% H ₃ PO ₄	0,003	0,001	0,011
		0,002	0,010	0,005
Zirconium dioxide	1% s. a. w. + 3% H ₂ O	0,004	0,002	0,012
		0,002	0,002	0,006
Corundum	The same	0,003	0,002	0,009
		0,004	0,002	0,030
Magnesium oxide	» »	0,003	0,002	0,010
		0,002	0,002	0,005

*The upper figure is the initial content, the lower figure the content in the metal in its final state.

decarburize it; this does not occur when zirconium dioxide is used [4, 6]. The experience gained in the use of linings of tamped zirconium masses [7, 8] has not yet been extensively utilized for smelting of steels, owing to the high cost of zirconium dioxide.

To select the composition of a zirconium mass for lining vacuum induction furnaces, ensuring a long service life of the crucibles, and to establish the influence of the lining composition on the quality of precision alloys, working in conjunction with the Institute of Precision Alloys (TsNIChM) the Ukrainian Scientific-Research Institute of Refractories has carried out research, the results of which are given in this article.

The meltings were performed in 8-kg crucibles, 150 mm in diameter, 215 mm high, with wall thickness 20 mm. The crucibles were made by hand tamping, in a special metal mold, of masses based on electro-melted zirconium dioxide stabilized with calcium oxide and calcium zirconate.

The masses of electromelted ZrO₂ and CaZrO₃ consisted of particles smaller than 5 mm, including 30% of the 5-2 mm class, 10% of the 2-0.5 mm class, 20% of the 0.5-0.09 mm class, and 40% of the -0.09 mm class. As binders we used H₃PO₄, calcium aluminozirconate and barium aluminozirconate cements [9-11], and sulfite-alcoholic waste (s. a. w.) [12].

The molded crucibles were dried at 120°C, the crucibles based on a phosphate binder were subjected to heat treatment at 300°C. The first melting (roasting) of 008ZhR iron was performed in air. The heating time was 17 min, the residence time of the liquid metal in the crucible was 30 min. Melting of the precision alloys was then performed. In the laboratory we melted several series of precision alloys of the Fe-Ni, Fe-Co, and Fe-Al systems.

Maximal resistance was displayed by crucibles of a tamped zirconium mass based on s. a. w. (Table 1). As shown in [13], these masses have a high deformability before failure and a high resistance to crack propagation. After the first meltings, as a result of their thin walls (20 mm), crucibles made from zirconium masses based on cements or a phosphate binder were completely sintered and lost their capacity to resist the propagation of cracks induced by thermal shocks (the crucibles were completely cooled after each melting). After 3-6 meltings, these crucibles displayed cracks and the tests were discontinued. Furthermore, crucibles made from masses based on a phosphate binder increased the phosphorus content of the metal from 0.002 to 0.01% (Table 2) and therefore cannot be recommended for melting precision alloys.

Petrographic analysis of the linings after service shows the presence of three zones: a working zone, transition zone, and least altered zone. Melting is accompanied by gradual saturation of the lining with iron oxides and the products of deoxidation, leading to the appearance of enhanced amounts of the vitreous phase and magnetite (see Table 1). In the working zone of crucibles made from masses based on cements or s. a. w., monoclinic ZrO₂ is completely stabilized and disappears, but in crucibles made from masses based on a phosphate binder, owing to combination of the CaO as phosphates we observe destabilization, agreeing with the data of Karaulov [14].

As noted in [6], as a result of the reaction of the fused metal with the crucible material in vacuum the refractory oxides and the binder materials may be reduced by the deoxidizer, leading to contamination of the

TABLE 3. Variation of the Magnetic Properties and Content of Nitrogen and Oxygen Present as Impurities in Alloys with the Crucible Material*

Alloy	Sheet thickness, mm	Initial mag. permeability $\mu_0 \cdot 0.79 \cdot 10^3$, H/m	Max. magnetic permeability $\mu_m \cdot 1.256 \cdot 10^{-6}$, H/m	Coercive force $H_c \cdot 1.256 \cdot 10^{-2}$, A/m	Hysteresis loop rectangularity $B_r/B_m, \dagger \%$	Mass fraction, %	
						N ₂	O ₂
Iron-nickel No. 1	0,35	2	10	0,15	0,94	0,015	0,002
	0,35	1,75	8	0,20	0,92	0,020	0,004
The same No. 2	0,35	Not deter.	25	0,024	0,94	0,010	0,001
	0,35		20	0,031	0,90	0,010	0,003
The same No. 3	0,20	150	48	0,02	Not deter.	0,017	0,002
	0,20	125	40	0,03		0,018	0,005
Iron-aluminum	0,20	8	2,7	0,03	> >	0,030	0,002
	0,20	6	2,6	0,04		0,030	0,004

*Zirconium (upper figure), magnesite (lower figure).

† B_r, residual induction; B_m, maximal induction.

metal. In this connection we investigated iron smelted in crucibles made from zirconium, corundum, and periclase masses.

In all cases, when iron was smelted in crucibles of zirconium dioxide based on s. a. w., its contamination by products of the crucible was virtually zero (see Table 2). During roasting of the crucible in the first flushing melting, s. a. w. binder, which contains sulfur, is completely burnt and the metal subsequently suffers no contamination by this element. However, when 008ZhR iron is smelted under the same conditions in crucibles of magnesium oxide or aluminum oxide (corundum) we observed contamination of the metal with magnesium (up to 0.050%) and aluminum (up to 0.030%), and the content of nonmetallic inclusions in the metal was enhanced.

On the basis of laboratory investigations, for tests on industrial melting of a number of brands of precision alloys at the experimental factory of TsNIChM in vacuum induction furnaces (metal capacity 20 and 50 kg), to make the crucibles we selected a tamped zirconium mass based on s. a. w. Tests of the zirconium crucibles were performed in parallel with those of fused magnesium oxide. Particular attention was paid not only to the durability of the crucibles and their behavior during melting, but also to the magnetic properties and technological effectiveness of the alloys.

To make the crucibles we used a refractory mass of grade PTsB-93 according to TU 14-8-62-72 of zirconium dioxide stabilized with calcium oxide (4%). We melted alloys of an iron and nickel basis with added silicon, titanium, vanadium, aluminum, and certain other elements. The crucible service life was high: 70-80 meltings as against 40-50 for crucibles of electromelted magnesium oxide.

After the meltings we investigated the quality of the metal melted in zirconium crucibles and investigated the changes which had occurred in the crucibles during melting.

Specimens were taken from the top, middle, and bottom of a crucible which had been used for 50 melts. According to spectral analysis data, after service the working zone of the crucible contained oxides of iron (~10%), chromium (~10%), magnesium and manganese (1-2%), aluminum (1-5%), calcium (~1%), titanium and vanadium (<<0.1%), and silicon (~1%). This indicates that the working zone of the crucible is saturated not only with iron oxides but also the products of deoxidation of the steel.

Together with the results of micro x-ray-spectral analysis, the petrographic analysis data enabled us to distinguish a general pattern of change in the crucible microstructure during reaction with the metal: Oxides of Ti, Ca, Mn, and Ni form a solid solution with ZrO₂. In the binder we observe crystallization of the silicate component, represented by SiO₂, zircon (ZrSiO₄), and cordierite (Mg₂Al₄Si₅O₁₈).

In the assessment of the quality of iron-nickel magnetically soft alloys, we established that melting in a zirconium dioxide crucible ensures the preparation of alloys with a lower impurity content and better magnetic properties than in the case of magnesium oxide crucibles (Table 3). The best results were obtained on difficultly deformable alloy 40KKhNMI for cores, and on iron-nickel and iron-aluminum high alloys.

The content of nonmetallic inclusions and harmful impurities in the metals in their final state was 1.5 times less than in alloys obtained in magnesite crucibles; this enhanced the technological characteristics and properties of the alloys. Thus these experiments on the use of tamped zirconium masses for making the

lining of vacuum furnaces for melting precision alloys indicate that these refractories are promising materials and can be recommended for extensive use in pilot plants and under industrial conditions.

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INFLUENCE OF SURFACE PHENOMENA ON CHOKING OF CHANNELS IN STEEL-POURING EQUIPMENT

V. P. Shevchenko, N. F. Nakonechnyi, UDC 66.028-033.76:669.18.046.518].001.5
R. Ya. Yakobshe, V. P. Osipov,
and V. A. Efimov

An important problem in metallurgy, and one which has not yet been solved, is to ensure that the channels of batchers in pouring equipment shall retain constant cross sections. There are a number of hypotheses concerning the mechanism of choking (overgrowth) of the nozzles, but none of them gives a satisfactory explanation of this phenomenon. Singh [1] has analyzed various views of the mechanism of this process, and has given additional experimental data which he explains from the viewpoint of the precipitation hypothesis. However, this hypothesis does not explain why corundum powder precipitated on the surface of a channel does not form a smooth layer, but often takes the form of separate branched projections [1, 2, etc.], which appear in the solidified metal in the form of irregularly shaped channels (Fig. 1).

The powder projections do not crumble and are not washed away by the flowing steel. The precipitation hypothesis also fails to explain why overgrowth of the channels is 5-10 times less intensive when corundum powder is added to the steel than when the corundum is formed by adding metallic aluminum to the steel [3].

As a result of investigations and observations, the present authors have come to the conclusion that overgrowth of batcher channels by the products of killing of the steel results from three processes: precipitation of a nonmetallic phase suspended in the steel; formation of oxides on the surface of the channel owing to injection of atmospheric oxygen through pores in the refractory and in breaks in the flow; and deoxidation of the steel on the surface of the refractory. The surface phenomena have a decisive influence.

On the basis of theoretical considerations [4], which have been confirmed experimentally [3, 5], we have analyzed the relative importance of these processes in the overgrowth mechanism and their relations with surface phenomena. With low concentrations of strong deoxidizers, the free energy of the system is insufficient for the formation of an interphase surface between the growing nonmetallic inclusion (i) and the steel

Institute of Problems in Casting, Academy of Sciences of the Ukrainian SSR. Translated from *Ogneupory*, No. 11, pp. 34-36, November, 1980.